

**SCIENTIFIC BENEFIT OF A HYPERVELOCITY MARS ATMOSPHERIC SAMPLE CAPTURE AND EARTH RETURN WITH THE SCIM MISSION.** Roger C. Wiens<sup>1</sup>, Mark H. Thiemens<sup>2</sup>, Laurie A. Leshin<sup>3</sup>, and Ben Clark<sup>4</sup>, <sup>1</sup>Los Alamos National Laboratory ([RWiens@LANL.Gov](mailto:RWiens@LANL.Gov)), <sup>2</sup>University of California, San Diego ([MHT@Chem.UCSD.Edu](mailto:MHT@Chem.UCSD.Edu)), <sup>3</sup>Arizona State University ([Laurie.Leshin@ASU.Edu](mailto:Laurie.Leshin@ASU.Edu)), <sup>4</sup>Lockheed Martin Astronautics ([Benton.C.Clark@LMCO.Com](mailto:Benton.C.Clark@LMCO.Com))

**Introduction:** Atmospheric and volatile measurements are crucial to understanding both Mars' climate history and its potential for harboring life. Our present knowledge of the Mars atmosphere comes primarily from the Viking mass spectrometers, gases trapped in the martian meteorites, and from telescopic observations. The Viking landers measured the chemical composition of all major atmospheric species [1,2], but gave only high-uncertainty results on a few isotopic compositions. Thus, most of what we believe about the composition of the martian atmosphere is inferred from the martian meteorites. Gases contained in several of these meteorites are thought to be unfractionated martian atmosphere trapped by shock implantation during ejection from Mars. However, the derivation of the Mars atmospheric composition is not straightforward, as the meteorites also appear to have retained magmatic gases, and contain cosmic-ray spallation products from their journey through space. Additionally, the martian atmosphere found in these meteorites was trapped some time in the past. An important MEPAG goal is the high precision measurement of the *present-day* atmosphere. The Sample Collection for Investigation of Mars (SCIM) mission, presently in a competed Phase A study, proposes to return 1 liter STP of the Mars atmosphere to Earth for isotopic study. Here we discuss the great importance of obtaining such a sample for analysis in terrestrial laboratories. A companion paper discusses the SCIM dust sample return science [3].

#### **Mars Atmospheric Science:**

*Stable Isotopes (O,C,N,H).* Comparison of oxygen and hydrogen isotopic compositions from gaseous and lithic sources can constrain the long-sought total primordial volume of water on Mars, and is key to understanding the surface-atmosphere interactions, and their relation to atmospheric escape. For example, most atmospheric isotope ratios strongly support the importance of atmospheric escape through time by recording heavy isotope enrichments due to preferential loss of the lighter isotopes from the atmosphere [e.g., 4]. However, the oxygen isotope ratio was found by Viking to be terrestrial (a result supported by martian meteorite analyses of lithic and hydrous phases), though with a Viking analysis precision of only  $\pm 10\%$ . The O isotope ratio can be determined in terrestrial laboratories to better than  $\pm 0.02\%$ , a factor of 500 improvement over Viking. A terrestrial-like O isotopic composition for the martian atmosphere would imply that oxygen in the atmosphere is buffered by a large non-atmospheric reservoir such as water or CO<sub>2</sub> in the polar caps or crust, or by crustal silicates, perhaps through the action of hydrothermal systems [5]. Unraveling the

mechanisms for such surface-atmosphere interactions demands very high-precision isotope measurements, as can be accomplished in terrestrial laboratories.

The situation for carbon is similar to oxygen in that it was measured to be terrestrial  $\pm 10\%$  based on Viking, suggesting buffering of the atmosphere by a larger reservoir. High-precision knowledge of the atmospheric C isotope ratio is critical to assessing possible martian biosignatures in organic matter from Mars.

Unlike C and O, the N isotopic composition was found by Viking to be strongly enriched in the heavy isotope, suggesting that  $\sim 99\%$  of the original atmospheric inventory has been lost to space [6]. The martian meteorites confirmed the <sup>15</sup>N enrichment, but only by plotting samples on a mixing line leading to the Viking measurement. The most <sup>15</sup>N-enriched martian meteorite samples are  $\sim 300\%$  [7,8], while the Viking measurement was  $620 \pm 160\%$ . This illustrates the great difficulty of trying to interpret the martian atmospheric composition directly from martian meteorite measurements.

*Noble Gases.* Recent discussion of the Ar-Kr-Xe ratios in martian meteorites [9] illustrates why new, high-precision measurements of martian atmospheric components are needed. The only measurement of the present-day atmospheric composition--Viking data--has an uncertainty greater than  $\pm 50\%$ . Analyses of gases trapped in the martian meteorites are more precise in their suggested Kr/Xe ratios, but they don't agree with each other. This disagreement--*by nearly a factor of 4* in some cases--encompasses Ar/Xe and <sup>129</sup>Xe/<sup>132</sup>Xe as well as the Kr/Xe. If this discrepancy is an artifact of the unknown provenance of the gas in the meteorite, there is no obvious process recorded. The differences have led to the suggestion that the Mars atmospheric Ar-Kr-Xe ratios are controlled by a larger near-surface clathrate reservoir, in turn controlled by climate [9]. The hypothesis in [9] is that the Mars atmospheric gases were incorporated into the various meteorites at different times and under different climatic conditions, under which differing amounts of these gases were locked up in the clathrates, leading to different Ar-Kr-Xe ratios in the atmosphere. While there may be other explanations for the differences in the martian meteorite noble gas ratios, this illustrates the difficulties of relying on meteorite data to understand the Mars atmosphere.

Noble gas *isotopic* ratios are instrumental in determining the time history of the martian atmosphere and climate. Neon and helium are lost from the atmosphere on medium to short timescales ( $\sim 10^8$  and  $\sim 5 \times 10^4$  years, respectively), while argon is lost on a longer ( $> 10^9$  year) timescale [4, 10-13]. We have

essentially *no measurements of the helium and neon isotope ratios, and only poor constraints on the argon isotopic ratios* [e.g., 14]. High precision measurement of all of these isotopes are required to elucidate the dynamic balance between volcanic degassing and atmospheric escape through time, a key ingredient in understanding the Mars climate through time. Additionally, radiogenic isotopes of  $^{40}\text{Ar}$  and  $^{129}\text{Xe}$  are particularly useful because they help constrain the early degassing history [e.g., 10, 15-17]. High precision measurements of atmospheric  $^{80}\text{Kr}$  and  $^{128}\text{Xe}$  might constrain globally averaged surface abundances of Br and I—paleo-ocean constituents—through time [15,16,18]. Ratios of  $^{134},^{136}\text{Xe}$ , will constrain the U/Pu ratio of Mars' interior [10,17,19]. Finally, high precision Kr and Xe isotope patterns from another earth-like planet will contribute to understanding the formation of the planets from the solar nebula [10,19,20].

**Carbon-14.** Radiocarbon illustrates the unique advantages of a returned sample. Mars atmospheric  $^{14}\text{C}$  potentially provides a check on recent exchange between atmosphere and regolith sources.  $^{14}\text{C}$  is produced in the atmosphere by cosmic rays, but it decays with a half-life of 5730 years. The atmospheric  $^{14}\text{C}/^{12}\text{C}$  ratio expected in the absence of recent atmosphere-surface interaction has been calculated [21,22]. A lower measured ratio would suggest that long-term regolith or polar cap sources have recently contributed “dead” (e.g.,  $^{14}\text{C}$ -poor) carbon to the atmospheric  $\text{CO}_2$ . A reasonable measurement of the  $^{14}\text{C}$  content can be obtained by accelerator mass spectrometry with as little as  $10^6$  atoms. It would be useful to detect  $^{14}\text{C}$  even if it was depleted in the Mars atmosphere by an order of magnitude by exchange with the surface reservoirs, though this level of depletion is unlikely. To make such a measurement, approximately  $5 \times 10^{-4}$  moles, or less than 20 ccSTP, of atmospheric gas is needed. This measurement will not be made in-situ, as the required instrumentation—an accelerator mass spectrometer—is currently one of the largest instruments used for geochemistry, weighing many tons.

**Hypervelocity Atmospheric Collection With SCIM:** Collection at hypervelocity and return of a Mars atmospheric sample has been previously proposed [23]. However, at relatively high altitudes, and correspondingly low gas pressures, it is difficult to avoid mass fractionation, even when collection is below the turbopause (~100 km), because the mean free path of atmospheric species is on the same order as the diameter of the collection orifice, leading to an enrichment of the light gases and isotopes. The SCIM mission avoids this with its relatively low descent to ~37 km, and by collecting gas at the stagnation point of the aeroshell, leading to gas pressures that are a significant fraction of a bar, and for which the molecular mean free paths are orders of magnitude smaller than the orifice diameter. Collection at the nose also avoids potential contamination by aeroshell ablation products. Collection is accomplished in two

independent systems, one completely passive system meeting the minimum collection requirements, and an additional, cryogenic system using off-the-shelf, multiple-flight-proven components. Together the two systems will provide more than 1 liter STP of the Mars atmosphere for terrestrial analysis, as well as a reservoir for use as future analysis techniques are developed.

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Table 1. Mars atmosphere measurement objectives for the SCIM mission

Measurement**	Current Knowledge	SCIM Precision
1 Ar/Kr/Xe	Viking ~±50% MM* ambiguous	± 2%
2 $^{17,18}\text{O}/^{16}\text{O}$	Viking ±10%	± 0.02%
3 $^{13}\text{C}/^{12}\text{C}$	Viking ±10% MM ambiguous	± 0.02%
4 D/H	Astro obs give diverse values; MM ~±20%	± 0.5%
5 $^{15}\text{N}/^{14}\text{N}$	Viking ±16% MM ~±10%	± 0.1%
6 $^{14}\text{C}/^{12}\text{C}$	NONE	± 10%
7 $^3\text{He}/^4\text{He}$	NONE	± 1%
8 Ne isotopes	NONE	± 0.2%
9 $^{36}\text{Ar}/^{38}\text{Ar}$	Viking ±30% MM ~±10%	± 0.1%
10 $^{40}\text{Ar}, ^{129}\text{Xe}$	Viking ±20-50%, MM ±1-5%	± 0.1%*
11 $^{128}\text{Xe}, ^{80}\text{Kr}$	Viking NONE MM ±1%	± 0.1%*
12 $^{134},^{136}\text{Xe}$	Viking NONE MM ±0.7%	± 0.1%*
13 Kr,Xe isotopes	MM ±0.7-3%	± 0.1%*

\*Relative to reference isotope; MM = martian meteorites

\*\*All measurements require < 1 cc STP of gas per analysis, except #6, which requires < 20 cc STP.